Renewable and Sustainable Energy Reviews 31 (2014) 61–70

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Recent development and economic analysis of glycerol-free processes via supercritical fluid transesterification for biodiesel production

Gaik Tin Ang [a], Kok Tat Tan [a,b], Keat Teong Lee [a,*]

[a] School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia
[b] Department of PetroChemical Engineering, Faculty of Engineering and Green Technology, Universiti Tunku Abdul Rahman, Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia

ARTICLE INFO

Article history:
Received 23 May 2012
Received in revised form
22 October 2013
Accepted 11 November 2013
Available online 8 December 2013

Keywords:
Biodiesel
Glycerol-free
Supercritical fluids
Transesterification

ABSTRACT

In this review, recent development of glycerol-free supercritical fluid transesterification for biodiesel production was discussed. Glycerol-free supercritical fluid processes including single-step and two-step transesterification for biodiesel production were reviewed and subsequently the advantages and limitations were highlighted. Value-added by-product from glycerol-free production such as triacetin is more profitable compared with glycerol produced in conventional biodiesel production. Furthermore, the quality of biodiesel could be enhanced with the presence of triacetin, which is co-produced in supercritical methyl acetate transesterification reaction. However, there are concerns regarding the huge energy required to conduct supercritical reaction at elevated temperature and pressure. Hence, economic consideration in terms of equipment needed and profit margin were discussed in order to study the profitability of glycerol-free supercritical biodiesel production in the industry. Results showed that glycerol-free supercritical dimethyl carbonate process has the highest profit margin, indicating that it is economically competitive and could provide larger revenue to biodiesel producers.

Contents

1. Introduction

Sustainable economic development depends substantially on continuous and steady supply of energy sources. For instance, transportation, agriculture and industrial sectors required huge

* Corresponding author. Tel.: +60 4 5996467; fax: +60 4 5941013.
E-mail address: chktlee@eng.usm.my (K.T. Lee).

1364-0321/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.rser.2013.11.004

amount of energy sources to accommodate their daily activities. Currently, the main energy sources employed by these sectors are non-renewable fossil fuels such as petroleum, coal and natural gas which inevitably lead to cost escalation and depletion in these natural resources. Furthermore, extensive combustion of fossil fuels also causes detrimental effects to the environment due to excessive emission of hydrocarbon particulates and greenhouse gases such as CO_2, NO_x, O_3 and CH_4 which leads to air pollution and global warming, respectively. Therefore, with alarming environmental degradation phenomenon and increasing awareness among the public regarding harmful effects of employing fossil fuels, researchers throughout the world have been focusing on developing a renewable, sustainable and clean source of energy to replace these natural resources.

One of the most researched renewable energy with enormous potential and prospect to be the main source of clean energy is biodiesel. Biodiesel is considered to be an environmental friendly source of energy because it is made from renewable sources and because of its lower emissions compared to fossil fuels. Biodiesel is derived from oil-bearing crops which absorb carbon from the atmosphere during photosynthesis process. Therefore, biodiesel has the potential to alleviate harmful emission during combustion process compared to fossil fuels as reported by Kumar and Nerella [1] that exhaust emissions in terms of CO, SO_2, and CO_2 compounds decreased with the increment of biodiesel percentage in biodiesel-diesel blend. Therefore, biodiesel could address the issue of energy security and sustainability without compromising our environment.

Refined vegetable oil or even waste cooking oil is commonly employed as the source of the triglycerides (TG) to produce biodiesel through transesterification reaction with alcohol in an alkaline homogenous catalytic system. The most common homogeneous catalysts are sodium hydroxide (NaOH) and potassium hydroxide (KOH). However, these processes may cause unwanted saponification reaction with free fatty acid which decreases catalyst efficiency and biodiesel yield [2,3]. Other than that, these processes may have to couple with an alkaline waste-water treatment in their production plant. Otherwise, untreated waste stream released to the drain could cause adverse effects to the ecosystems. Therefore, numerous methods have been carried out to solve these problems, such as heterogeneous catalysts [4], lipase-catalyzed transesterification [5] and non-catalytic supercritical alcohol transesterification [6,7]. Among these methods, non-catalytic supercritical fluid transesterification has been found to have numerous advantages of being simpler, producing higher yield in a short period of time and easier purification in biodiesel production.

Recently, biodiesel production from vegetable oils has been extensively studied via supercritical fluid transesterification. This novel technology of converting vegetable oil to biodiesel via non-catalytic supercritical alcohol was initially reported by Saka and Kusdiana [6]. The overall transesterification reaction for TG with 3 mol of methanol is shown in Eq. (1). Transesterification reaction refers to a common process of exchanging acyl ($RnCO^-$) group between fatty acid and alcohol. In this reaction, methanol is the acyl acceptor of group found in triglycerides to form fatty acid methyl esters (FAME) and glycerol:

$$\text{Triglycerides} + 3\text{Methanol} \leftrightarrow 3\text{FAME} + \text{Glycerol} \tag{1}$$

It is well known that supercritical methanol process has high reaction rate which allows the reaction to be completed in a short period of time. It is also simpler in its products separation and purification procedure as there is no catalyst in the system. By using supercritical reaction, the existence of high free fatty acids (FFA) and water content in oils/fats do not affect the yield or conversion. Instead, it was found that they enhance the formation of methyl esters as the FFA were also converted to methyl esters as reported by Kusdiana and Saka [8] and Tan et al. [9]. Hence, waste cooking oil which commonly consists of high FFA percentage and water could be employed in supercritical fluid transesterification method without any pre-treatment [10]. This finding shows the superiority of supercritical alcohol technology in producing biodiesel compared to conventional methods which require pre-treatment of oils to reduce the water content.

Biodiesel production has experienced a major surge in developed countries such as Germany, Italy, France and United States, as well as in developing countries such as Argentina, Indonesia and Malaysia. Biodiesel production in the world increased substantially from 2.2 million tons in 2002 to an estimated 11.1 million tons in 2008 [11]. In biodiesel production, crude glycerol is the major by-product from the conventional transesterification with the amount produced is approximately 10 wt% of oils/fats employed in the reaction [12]. Consequently, with the huge production of biodiesel throughout the world, excessive crude glycerol has been produced which leads to significant price decline in the world's market [13]. Other than that, the major problem with glycerol in biodiesel production is the contamination of methanol which makes it unsuitable to be processed for consumer market. The only treatment that could refine crude glycerol to pharmaceutical grade is by employing high temperature low pressure distillation [14] which is very costly and uneconomical for this low cost commodity. Even in supercritical alcohol transesterification [15–19], this unprofitable crude glycerol will be produced together with biodiesel. Therefore, in order to improve the economics of biodiesel processing as well as to eliminate waste glycerol in the production stream, some alternative methods need to be carried out, either replacing or transforming crude glycerol into other value-added commodities [20–23].

One of the methods is by employing non-alcohol reactant in the reaction which could produce other invaluable by-product instead of the unwanted glycerol. Glycerol-free process via supercritical fluid transesterification was initially reported by several researchers [21,24,25] by replacing the reactant of alcohol in conventional supercritical transesterification with methyl acetate and dimethyl carbonate. This breakthrough research had initiated a lot of researches in this glycerol-free process via supercritical fluid transesterification for biodiesel production. Therefore, this study aims to review recent progress of glycerol-free supercritical fluid processes including single-step and two-step reaction for biodiesel production and subsequently highlights their advantages and weaknesses. Apart from that, economic analysis will also be discussed in order to examine the profitability as well as potential of glycerol-free supercritical biodiesel production in the industry.

2. Glycerol-free process via supercritical fluid technology

Glycerol-free processes via supercritical fluid technology are basically divided into two methods which are single-step and two-step supercritical fluid transesterification. In single-step supercritical fluid transesterification, reaction takes place only once after the heating of reactant up to its critical temperature and pressure with TG. In two-step subcritical-supercritical fluid transesterification, TG is first induced to FFA and by-product in the hydrolysis reaction. Subsequently, the obtained FFA undergone esterification reaction and produce FAME in supercritical fluid reaction. In this two-step supercritical method, reaction condition is relatively milder with lower operating temperature and pressure.

2.1. *Single-step supercritical fluid*

It is well known that supercritical fluid transesterification reaction requires high temperature above the critical temperature

of reactant. Dimethyl carbonate (DMC) and methyl acetate (MA) are commonly used as the reactant in single-step glycerol-free supercritical fluid process. The critical pressure and critical temperature of DMC are 4.63 MPa and 274.9 °C, respectively [26]. On the other hand, the critical pressure and temperature of MA are 4.69 MPa and 233.7 °C, respectively. Other than MA, various types of carboxylate esters had been utilized by Goembira et al. [27] to produce glycerol-free biodiesel.

2.1.1. *Dimethyl carbonates as the reactant*

In order to revalorize glycerol into glycerol carbonate (GC) which is useful in enormous application, dimethyl carbonate (DMC) was chosen in one-step glycerol-free supercritical fluid transesterification biodiesel production. DMC is a versatile reactant, non-toxic and biodegradable that could be synthesized via an environmentally friendly process [24,26,28]. Ilham and Saka reported that TG could be converted into FAME by reacting it with DMC. In their study, all experimental works were conducted in a 5 ml Inconel-625 reaction vessel. In the transesterification reaction, TG of rapeseed oil was treated with DMC to oil in a molar ratio of 42:1 mol/mol in supercritical condition at 350 °C/20 MPa within the period of 3–15 min. After the reaction was completed, the reaction vessel was then moved into a water bath to stop the reaction. The reaction mixture was then separated into upper and lower portions after the evaporation of DMC. They concluded that transesterification reaction goes through a three stepwise reactions. Initially, TG reacts with one molecule of DMC to produce methyl carbonate diglycerides (MCDG). Then, the MCDG will further react with one molecule of DMC to produce dimethyl carbonate monoglyceride (DMCMG). Finally, DMCMG again react with one molecule of DMC to produce FAME with GC and citramalic acid as by-products. The proposed overall transesterification between TG and DMC reaction is shown in Eq. (2). After 12 min of reaction, rapeseed oil with molar ratio at 42:1 mol/mol of DMC to oil that operated at 350 °C/20 MPa was successfully converted to FAME, GC and citramalic acid with FAME yield of 94%.

$$\text{Triglycerides} + 3\ \text{DMC} \leftrightarrow 3\ \text{FAME} + \text{Glycerol carbonate} + \text{Citramalic acid} \quad (2)$$

Lately, Ilham and Saka [28] had carried out an optimization study on all the important parameters such as reaction temperature, pressure, time, molar ratio of DMC to oil based on the FAME yield, thermal decomposition, degree of denaturation, tocopherol content, oxidation stability and fuel properties. According to their report, reaction pressure gives significant effect on the biodiesel yield especially in the SCDMC reaction. This is because DMC could decompose to CO_2 and methanol at the low pressure at 5 MPa and 10 MPa, while remained stable at higher pressure at 20 MPa and 40 MPa [29]. Therefore, FAME yield as high as 96 wt% could be achieved for the operating pressure at 20 MPa and 40 MPa at 300 °C reaction temperature for 30 min. Other than that, thermal stability of methyl esters was evaluated on their exposure at various supercritical conditions. From there, saturated FAME such as methyl palmitate and methyl stearate were stable at the operating temperature at 300 °C/20 MPa, however they were started to decompose after prolonged reaction time for 60 min at 350 °C/20 MPa. For the unsaturated FAME such as methyl oleate, methyl linoleate and methyl linolenate, they were decomposed significantly for the operating temperature at 350 °C/20 MPa [30]. Other than that, tocopherol is important to prevent oxidation in biodiesel so that it could be stored for a longer time. In their study, tocopherol is stable and remained unchanged at milder condition at 300 °C/20 MPa whereas decrease drastically at severe temperature at 350 °C/20 MPa. Therefore, the optimum condition for supercritical DMC was determined at 300 °C/ 20 MPa, 20 min/42:1 M ratio of DMC to oil to have satisfactory 97.4 wt% FAME yield.

Other than that, Tan et al. [31] also investigated the DMC reaction with palm oil as the feedstock of biodiesel via supercritical technology. In their study, supercritical DMC reaction was carried out in a 12 ml stainless steel Super Duplex® batch reactor which can sustain high temperature and pressure. The working temperature and pressure employed in their study were covering up to 400 °C and 25 MPa, respectively. Moreover, response surface methodology (RSM) analysis was carried out in their studies to achieve the optimum conditions of the affecting factors that are molar ratio of DMC to oil, temperature and reaction time. The mathematical model developed in their report was statistically significant and adequate to predict optimum yield for the biodiesel production from palm oil with DMC. The optimum condition in their supercritical palm oil–DMC process was found to be 380 °C for reaction temperature, 39:1 mol/mol of DMC to oil molar ratio and 30 min of reaction time to obtain 91% optimum yield of biodiesel.

2.1.2. *Carboxylate ester as the reactant*

Other than DMC, carboxylate ester such as methyl acetate (MA) was initially chosen as reactant in glycerol-free process via single-step supercritical fluid interesterification by Saka and Isayama [21]. Interesterification refers to a reaction of exchanging acyl group between two different ester compounds; in contrast to transesterification which involves exchanging of acyl group between fatty acid with alcohol. In their study, it was found that supercritical interesterification reaction of rapeseed oil with MA without catalyst can produce FAME and triacetin (TAG). The supercritical fluid interesterification reaction was carried out at temperature range of 270–380 °C and pressure of 20 MPa with reaction time ranging from 10 to 120 min while the molar ratio was fixed at 42:1 mol/mol of MA to rapeseed oil. It was reported that interesterification goes through three reversible sequential reactions. First, TG and one molecule of MA react, generating one molecule of monoacetylglyceride (MAG) and FAME. In the same way, diacetyglyceride (DAG) and FAME are generated from MAG and MA. Finally, TAG and FAME are generated from DAG and MA. The overall reaction of TG with 3 molecules of MA is shown in the following equation:

$$\text{Triglycerides} + 3\text{Methyl acetate} \leftrightarrow 3\text{FAME} + \text{Triacetin} \quad (3)$$

From their results, 97% yield of FAME can be achieved after TG react with MA for 45 min at 350 °C. However, when longer reaction period is employed, the yield of FAME was found to be lower. Other than that, mixture of FAME and TAG could be employed as biodiesel fuel (BDF). In conventional alcohol-based transesterification, FAME is the only product for biodiesel fuel since glycerol is produced as the unprofitable by-product. As the molar ratio of FAME/TAG in product mixture is 3:1 (mol/mol) which is equivalent to 4:1 in mass ratio (w/w), the theoretical weight of biodiesel (FAME+TAG) is 125%, instead of 100% in supercritical methanol transesterification. In their study, they achieved the production yield of BDF at 105%, which is higher than the maximum BDF yield of 100% (FAME only). In other words, there are more BDF that can be produced from one unit of rapeseed oil.

Goembira and Saka [32] also carried out optimization of supercritical MA on rapeseed oil on the important affecting parameters of reaction temperature, pressure, time and molar ration based on the production yield, degree of thermal decomposition, *cis–trans* isomerization and tocopherol content. The highest yields of 96.7 wt% of FAME and 8.8 wt% of TAG were obtained at operating condition of 350 °C/20 MPa/ 45 min/1:42 oil to methyl acetate molar ratio [33].

This breakthrough research by Saka and co-workers has initiated a lot of subsequent researches in this SCMA technology using different vegetable oils feedstock. For instance, Campanelli et al. [34] carried

out a study to convert edible, non-edible oils and waste cooking oil to biodiesel by using supercritical MA technology. The oils that were investigated include soybean, sunflower, *Jatropha curcas* and waste soybean oil. In his study, all experimental works were conducted in a 100 ml stainless steel vessel equipped with a stirrer. Their reactor was able to operate in the pressure range covering up to 10–30 MPa and also temperature range with 300–345 °C. The molar ratio of the MA to oil was varied between 25:1 and 59:1 mol/mol. A complete conversion (100%) to FAME was achieved after 50 min at 345 °C, 20 MPa and with molar ratio of MA to oil at 42:1.

Other than that, Tan et al. [35] carried out optimization study for production of biodiesel by supercritical MA by using palm oil as biodiesel feedstock. In their study, FAME together with the TAG has been successfully derived from interesterification reaction. The effects of molar ratio, reaction temperature and reaction time on the yield of biodiesel were optimized by using response surface methodology (RSM) analysis. The optimum conditions were found to be 399 °C for reaction temperature, 30:1 mol/mol of MA to oil molar ratio and reaction time of 59 min to achieve 97.6% biodiesel yield.

Next, Niza et al. carried out the SCMA on another oil feedstock that is *J. curcas* oil [36,37]. In their study, a comparison study between supercritical methyl acetate (SCMA) and supercritical methanol (SCM) was reported. Both reactions were compared and optimized by using response surface methodology (RSM) analysis. For the SCM reaction, a yield of 89.4% was achieved within the reaction time of 27 min, reaction temperature of 358 °C, and methanol-to-oil molar ratio of 44. Whereas, for SCMA reaction, a yield of 71.9% was obtained within the reaction time of 32 min, reaction temperature of 400 °C and methanol-to-oil molar ratio of 50. Other than the optimization study, Niza et al. also carried out thermal stability study for methyl esters such as methyl oleate and methyl linoleate and triacetin in SCMA reactor [37]. In their report, thermal degradation of methyl oleate is significant at temperature 390 °C and above, meanwhile methyl linoleate significantly degrade at temperature 390 °C to give less than 50% recovery. TAG was also found not to be thermally stable at temperature 360 °C. Therefore, it is preferable to conduct SCMA reaction at temperature lower than 360 °C to give a better quality of BDF. Niza et al. had also carried out the effect of impurities such as water and FFA in SCMA and SCM reactions [38]. Both reactions are showing a high tolerance to the impurities with consistent high yield in FAME. Whereas, SCMA reaction had a better advantage as it produced more valuable by-product which is TAG compared to SCM reaction.

Other carboxylate esters such as methyl propionate, methyl butyrate, ethyl acetate, ethyl propionate, ethyl butyrate, propyl acetate, propyl propionate, propyl propionate, propyl butyrate, butyl acetate, butyl propionate and butyl butyrate had been used as reactant with triglyceride to produce fatty acid alkyl esters by Goembira et al. [27]. Rapeseed oil was used as the feedstock of TG. TG was converted into fatty acid alkyl esters (FAAE) and triacins via supercritical interesterification carboxylate esters as shown in Eq. (4). The highest product (FAME and TAG) yield of 97.7 wt% was achieved by SCMA among the supercritical carboxylate esters with reaction temperature at 350 °C and pressure 17.8 MPa. For the other carboxylate esters, yield of FAME was significantly low compared with methyl acetate. This is due to the longer alkyl chains in the other carboxylate esters that reduced the reactivity between TG with esters.

$$\text{Triglycerides} + 3\ \text{Carboxylate ester} \leftrightarrow 3\ \text{FAAE} + \text{Triacin} \quad (4)$$

Other than that, SCMA need a longer reaction time to give a slightly lower yield compared with SCM and SCDMC reaction [27]. This is because methyl acetate is considered as weakly polar solvent, thus it has lower reactivity and needs a longer reaction time compared with other reactants such as methanol and dimethyl carbonate. With the longer reaction time, high degree of decomposition of FAME could occur and hence giving a lower yield in SCMA. Therefore, methods to increase the reactivity of SCMA should be further studied in future works. However, triacins in FAAE had improved some important fuel properties such as pour point and cold filter plugging point which suggesting SCMA can give a prospective alternative in biodiesel production.

Lately, biodiesel production using SCMA had been carried out by Dona et al. in a tubular packed bed reactor with soy bean oil and macauba oil as TG feedstock [39]. Interesterification reaction was carried out in 57.7 ml tubular reactor that made of stainless steel tubing and packed with glass beads with diameter 2.5 mm. Initially, MA and oil were mixed according to the mass ratio and stirred continuously in a closed flask. The mixture of oil and MA were fed into the reaction system by a high-pressure liquid pump (Acuflow). Reactor was placed in furnace with proper temperature controller. Effects of reaction temperature (300–400 °C), oil to MA mass ratio (1:2–1:5) and reaction time (18–45 min) were investigated at constant pressure 20 MPa. According to their results, the highest ester yield was obtained at 83% with a minimum decomposition of 17% at 325 °C, 1:5 and 45 min by macauba oil. Whereas, for soy bean oil, the highest ester yield was achieved at 44% at temperature 350 °C with oil to MA mass ratio of 1:5 and 45 min of reaction time; with a decomposition of 48% was achieved. The higher FFA content in macauba oil makes macauba oil gave a better yield in supercritical MA.

2.2. Two-step subcritical and supercritical fluid

In order to have milder experimental conditions for supercritical fluid transesterification, Saka et al. [13] proposed two-step supercritical methanol method for biodiesel production. Acetic acid was used as the reactant in the first step subcritical hydrolysis. The critical pressure and critical temperature for acetic acid are 5.80 MPa and 317 °C, respectively. In their research, the hydrolysis reaction of TG is firstly induced in subcritical acetic acid to fatty acids and TAG as shown in Eq. (5). The obtained fatty acid was then subjected to supercritical esterification reaction with methanol to produce FAME as shown in Eq. (6). Using a subcritical processing state at 300 °C/ 20 MPa for the first step (Eq. (5)), a yield of 91% of fatty acid and 85% of TAG were obtained after 30 min reaction. While using a supercritical esterification processing state at 270 °C/ 17 MPa for the second step (Eq. (6)), a yield of 97% of biodiesel was produced after 15 min reaction time.

$$\text{Triglycerides} + 3\ \text{Acetic acid} \leftrightarrow 3\ \text{Fatty acids} + \text{Triacetin} \quad (5)$$

$$\text{Fatty acids} + \text{Methanol} \leftrightarrow \text{FAME} + \text{Water} \quad (6)$$

The hydrolysis reaction between acetic acid and TG was reported to go through three sequential stages. Initially, TG reacts with one molecule of acetic acid to generate one molecule of monoacetyl diglyceride (MADG) and fatty acid. Similarly, diacetyl monoglyceride (DAMG) and fatty acid are generated from MADG and acetic acid. Lastly, TAG and fatty acid are generated from DAMG and acetic acid. Apart from that, they also compared the performance of transesterification reaction using methanol and MA with acetic acid. The reactivity of acetic acid was found to be higher than methanol and MA. This is because the excessive acetic acid and its acidity act as an acid catalyst in the first step transesterification reactions. Hence, reaction rate for the subcritical acetic acid with TG was higher than those of methanol or MA with TG.

Other than subcritical acetic acid, Ilham and Saka [40] also carried out two-step subcritical-supercritical DMC for *J. curcas* oil to produce biodiesel. In their first step, the hydrolysis of TG was carried out in subcritical water. TG was hydrolyzed in subcritical water to produce fatty acids and glycerol with high temperature and high pressure at

Table 1
Summary of the single-step of glycerol-free process via supercritical technology.

Oil feedstock/solvent	*T* (°C)	*P* (MPa)	ROH:TG (molar)	Reaction time (min)	Reactor	Maximum conversion (%)	Products	Ref.
Rapeseed/DMC	350	20	42	15	Batch	94	FAME GC Citramalic acid	[24]
Rapeseed/DMC	300	20	42	20	Batch	97.4	FAME GC Citramalic acid	[28]
Palm/DMC	380	–	29	30	Batch	91	FAME GC	[31]
Rapeseed/MA	350	20	42	45	Batch	97	FAME Triacetin	[21,32,33]
Jatropha/MA	345	20	42	50	Batch	100	FAME Triacetin	[34]
Palm/MA	390	–	30	59	Batch	97.6	FAME Triacetin	[35]
Jatropha/MA	400	–	50	32	Batch	71.9	FAME Triacetin	[36]
Macauba/MA	325	20	50	45	Continuous	83	FAME Triacetin	[39]

Table 2
Summary of the glycerol-free process via two-step subcritical-supercritical technology.

Researches	Saka et al. [13]	Saka and Isayama [21]
Feedstock	Rapeseed oil	*Jatropha curcas* oil
Reactant used in subcritical condition	Acetic Acid	Water
Temperature (°C)	300	270
Pressure (MPa)	20	27
Reaction time (min)	30	25
Product	FFA Triacetin	FFA Glycerol
Reactant used in supercritical condition	Methanol	DMC
Temperature (°C)	270	300
Pressure (MPa)	17	9
Reaction time (min)	15	15
Product	97% FAME 20% Triacetin	97% FAME Glyoxal

270 °C and 27 MPa, respectively. Fatty acids were extracted from the upper portion of the treated mixture while the lower portion was found to contain water and glycerol compounds. Subsequently, fatty acids were esterified in supercritical DMC at temperature of 300 °C and pressure of 9 MPa for 15 min to obtain 97% of FAME. Similar to first reaction, the products in the second reaction were allowed to separate into two layers where FAME was extracted from the upper portion while glyoxal in water was found in lower portion. Overall, FAME or biodiesel was produced as the main product while glycerol and glyoxal were produced as by-products. The second step of esterification could be modified by using supercritical methanol (270 °C/ 17 MPa) as shown in Eq. (6) where the product would be FAME and water. Nevertheless, their research has shown the possibility of producing glyoxal which has a potential commercial application in perfumery, flavor, pharmaceutical and agrochemical industries.

3. Advantages and disadvantages of glycerol-free process via supercritical technology

After reviewing the single-step and two-step glycerol-free process via supercritical technology, advantages and disadvantages of these methods will be discussed in terms of utilization potential and value of by-products, flexibility of oil feedstock and energy consumption. Table 1 highlights the optimum condition and products for single-step glycerol-free process supercritical fluid transesterification/interesterification from different researches. On the other hand, Table 2 summarizes the optimum condition and their respective products for two-steps glycerol-free process supercritical fluid transesterification.

3.1. Potential and value of by-products

In the single-step glycerol-free processes, TAG and glycerol carbonate (GC) were produced in supercritical MA and DMC technology, respectively, other than high percentage of biodiesel. TAG is commonly used as food additive, for instance as a solvent in flavoring and for its humectants function. In order to reduce engine knocking in fossil fuels, TAG can also be added as antiknock agent in engine and it can improve combustion properties of the biodiesel.

In supercritical DMC technology, GC and weak acids such as citramalic acid are produced as value-added by-products. GC is commonly used as substitution for petro-derivative compounds such as ethylene carbonate or propylene carbonate in synthesizing polymers such as polyesters, polycarbonates, polyurethanes and polyamides, surfactants and lubricating oils [41]. Other than that, GC can also be used to synthesis glycidol compounds which are widely used in the textile, plastics, cosmetics and pharmaceutical industries. Adding more to the list, glycerol carbonate can be used in semiconductor industries as electrolytes, solvents in lithium ion batteries [22] and even can be used in the CO_2 separation membranes as replacement to ethylene and propylene carbonates [42]. Other than that, if citramalic acid could be obtain from the glycerol-free biodiesel production in high purity, it is a valuable commodity in pharmaceutical and cosmetic industries since it can be used to reduce skin wrinkle and reverse the effect of aging on human facial [43].

In two-step subcritical–supercritical technology, TAG and glyoxal were produced in subcritical acetic acid and subcritical water technology, respectively. Commercial glyoxal is commonly supplied in aqueous solution. It is produced from the oxidation of ethylene glycol with silver or copper catalyst. Glyoxal is commonly used as crosslinking agent in textiles to produce softer and less wrinkled fabric. Other than that, it can also be used in the cosmetics components as a starting material with ureas for wrinkle-resistant chemical treatments. In glycerol-free biodiesel production, glyoxal is produced in the aqueous solution which is ready to be used in other applications. The prices of TAG, glycerol carbonate and glyoxal in 40% aqueous solution are much higher than glycerol itself. In order to increase the revenue for biodiesel manufacturers, economic analysis for the potential by-product should be taken into consideration.

3.2. High process flexibility of feedstock conditions

In conventional homogeneous alkaline catalytic transesterification, water and free fatty acid content in the oil feedstock can create a major problem [44]. The presence of water in the oil feedstock can cause hydrolysis of the formed FAME back to FFA [45]. Moreover, water will hydrolyze TG to diglyceride and FFA at higher temperatures. Therefore, pre-treatment on the feedstock to remove the water and FFA is necessary to prevent saponification reaction occurred. The allowance for FFA percentage in the well known homogenous alkaline NaOH/KOH catalytic transesterification is less than 1% [46]. Whereas, by using glycerol-free supercritical technology, various feedstock even waste cooking oil can be used without having the water and FFA problem. As reported by Niza et al. [38], the impurities of water and FFA do not give any detrimental effects to the product yield. The presence of water in SCMA reaction will induces hydrolysis of TG to produce FFA and glycerol. Subsequently, FFA will be esterified by MA to produce FAME and acetic acid. Then, glycerol will react with acetic acid to produce triacetin and water.

While FFA in the SCMA system, it will be esterified to produce FAME and water, in which water as the side-product could help in the hydrolysis of TG process and subsequently improved the biodiesel production yield [9]. Hence, cheaper feedstock such as non-edible oils, waste cooking oils and even unrefined crude oils with high FFA content can be used in this glycerol-free supercritical fluid biodiesel production.

3.3. High energy consumption

Higher energy consumption has become the only weakness of glycerol-free supercritical technology. In renewable energy field, there are concerns that the energy utilized in the process is more than the energy provided by biofuels obtained from glycerol-free supercritical technology [47]. In other words, more energy is required to produce per unit of FAME which has less energy content. Therefore, in glycerol-free supercritical technology, energy consumption and cost effective should be taken in to consideration before it can be completely commercialized in the industry.

In the two-step glycerol-free supercritical fluid transesterification, the operating temperatures were 300 °C and 270 °C for the subcritical acetic acid and supercritical methanol, respectively. On the other hand, for the subcritical water and supercritical DMC, the operating temperatures were 270 °C and 300 °C, respectively. The operating temperatures were slightly lower in the second step of the two-step supercritical methanol and supercritical DMC as shown in Table 2 compared with the single-step supercritical methanol and supercritical DMC shown in Table 1. These processes were milder in their operating temperature and pressure. However, the energy usage for two-step supercritical technology might be higher than single-step supercritical technology due to repeated heating and cooling in the former process.

4. Effect of triacetin (TAG) in biodiesel quality

Biodiesel is well known for its sustainability, non-toxic and biodegradable alternative fuel that has been used in transport and industry sectors. It reduces emission of greenhouse gases and has a higher flash point compared with petroleum-based diesel. The higher flash point has made biodiesel safer in transportation, storage and handling [48]. However, the lower heating value, higher viscosity and density of biodiesel could cause some problems when it is used in unmodified engine [49]. In order to improve the combustion and emission of engine, biodiesel can be added with some additives such as TAG [50]. Therefore, biodiesel properties such as density, kinematic viscosity, pour point and heating values are important factors to be taken into consideration in order to improve the engine performance.

The density of a fuel will affect fuel consumption and efficiency of fuel atomization. The density of fossil diesel is 800–850 kg/m^3 while biodiesel has value ranging from 860 to 900 kg/m^3. In the study by Saka and Isayama, [21] and Casa et al. [50], the addition of TAG causes increment in density of biodiesel fuel. According to American society for Testing and Material (ASTM) D6751 guidelines, there is no limit range for biodiesel fuel density. Thus, the percent addition of TAG in biodiesel is not limited according to ASTM D6751. However, according to the EN14214 guidelines, range for desired density is limited in the range of 860–900 kg/m^3 which indicates that maximum addition of TAG is 10 wt% in biodiesel produced from vegetable oils [50].

Viscosity has an important impact on fuel injection and combustion. It is an index expressing the stickiness of a fuel. The kinematic viscosity is important to be regulated within in a safety range at 3.5–5 mm^2/s and 1.9–6 mm^2/s for the EN14214 and ASTM D6715 regulation, respectively. Biodiesel with high kinematic viscosity will cause the fuel unable to be sprayed in the ignition chamber; while low kinematic viscosity will reduce the lubrication effect of biodiesel in the combustion engine. In the work by Saka and Isayama [21], kinematic viscosity against concentration of TAG in methyl oleate as biodiesel reference was studied. The kinematic viscosity was found to increase with addition of TAG in biodiesel. From their study, kinetic viscosity of 4.5 mm^2/s was achieved with 20 wt% of TAG in BDF which is well within the viscosity range for EN14214 standard and similar with those reported by Casas et al. [50].

Pour point of biodiesel is defined as the lowest temperature at which a liquid can flow under gravity. Fuels with high pour point

Table 3
Comparison of the fuel properties of the BDF with the biodiesel standards.

Property	Unit	ASTM D6751	EN14214	Model BDF [21,50]	Remarks (maximum triacetin)
Density (15 °C)	kg/m^3		0.86–0.90	0.914–0.921	≤10 wt% according to EN14214 Exact limit varies with different type of biodiesel
Kinematic viscosity (40 °C)	mm^2/s	1.9–6	3.5–5	4.2–4.6	≤20 wt%
Pour point	°C			10 (Palm) −21(Rapeseed)	Varies with different type of biodiesel
Flash point	°C	≥130	≥101	158–160	≤20 wt%
Cold filter plugging point	°C		≥−10 (Winter) ≥0 (Summer)	11 (Palm) −8 (Rapeseed)	Addition of TA will negatively affect CFPP Only beneficiary to Palm BDF Varies with different type of biodiesel
Cetane number		≥47	≥51	48–53	≤20 wt% according to ASTM ≤10 wt% according to EN14214 Exact limit varies with different type of biodiesel

are unsuitable to be used in cold regions as fuel will congeal and stop flowing under its own weight. Saka and Isayama [21] reported a decrease of 2 °C for a mixture of methyl oleate as the biodiesel reference and 20 wt% of TAG. In the study of Casas et al. [50], the effect of adding TAG on the pour point value was studied for different biodiesel feedstocks. The pour point for rapeseed biodiesel and palm biodiesel decreased about 9 °C and 3 °C, respectively, with addition of 20 wt% TAG. With the decreasing pour point value of BDF, it would be favorable because biodiesel could then be widely used in the cold regions without giving trouble to the engine.

Higher heating value (HHV) of biodiesel is the amount of heat released during combustion of a specific amount of biodiesel. HHV is measured in units of energy per mass of biodiesel. This parameter is very important for combustion engine because it is related to the consumption of fuel. TAG has a lower HHV value compared with biodiesel as there is higher oxygen content in TAG. From the study by Casas et al. [50], a 10% decrease (on basis of mass) in HHV value was achieved with the addition of 20 wt% TAG in biodiesel. In diesel engine, a fixed volume of fuel is injected into the engine. Thus, a higher density fuel (TAG blended in biodiesel) which may leads to a higher amount of fuel injected will release more energy during combustion. Although TAG has lower HHV (on the basis of mass) than biodiesel or diesel, its higher density increase the HHV of their mixtures expressed on the basis of volume. Table 3 shows the comparison of the fuel properties with the maximum TAG content in the biodiesel in relative to biodiesel standards. Hence, it has been proven that by adding TAG in most biodiesel blend, the quality of combustion could be enhanced.

5. Economic analysis

In order to show the benefits of glycerol-free biodiesel process, economic analysis is essential to shows the basic profits for the glycerol-free compared with the conventional supercritical methanol method. Economic analysis is carried out based on the cost of equipment involvement as well as cost of raw material and products.

5.1. Cost of equipment

In conventional supercritical methanol (SCM) production method, the biodiesel production plant can be divided into transesterification sections, biodiesel purification section and glycerol recovery section [51,52]. On the other hand, glycerol recovery process is not needed in glycerol-free supercritical methyl acetate (SCMA) and supercritical dimethyl carbonate (SCDMC) process. A simplified block flow diagram of SCM, SCMA and SCDMC is shown in Fig. 1(a)–(c), respectively. Apparently, a settler and a distillation column are necessary to recovery glycerol in SCM product stream. A settler is used to separate glycerol–methanol mixture with FAME while a distillation column is used to recycle excessive methanol from glycerol mixture and recover high purity of glycerol. For SCMA and SCDMC processes, products from transesterification do not required a settler to separate excessive MA or DMC with biodiesel as they are miscible with untreated triglyceride and FAME. Hence, thermal energy is needed in evaporator to recycle the excessive MA or DMC into the feed tank.

In SCMA production process, TAG is produced together with FAME. As discussed previously, 20% of TAG in FAME can effectively improve the combustion quality of FAME. Therefore, energy usage in this glycerol-free process can be reduced since the capacity of distillation is substantially lower than SCM process. Next, in SCDMC process, glycerol carbonate (GC) and citramalic acid is produced with FAME. After the recycle of DMC were conducted by employing evaporator, separation of glycerol carbonate (GC) from the FAME can be done easily as GC is not miscible with FAME. Hence, no extra energy is needed to separate GC from FAME since a settler could perform separation between GC and FAME.

Moreover, in glycerol-free biodiesel production, cost for fabricating distillation column for recovery glycerol can be reduced. Distillation columns are well known for their high operating cost in terms of fabrication, installation and even during maintenance. As a conclusion, by comparing the cost of equipment in the transesterification between SCM with glycerol-free SCMA and SCDMC processes, glycerol-free process is more economical as there is less equipment involved in the biodiesel production.

5.2. Cost of raw materials and products

In order to increase the economic potential of biodiesel production, it is important to study the economic value of the potential by-products. Table 4 shows the price for various by-products from supercritical fluid technology and also additive of biodiesel that is available in the market. On the other hand, prices for reactants and by-products in the transesterification reaction are shown in Table 5. In Table 4, it is clearly shown that the price for pure glycerol is the lowest among all the by-products. Moreover, glycerol produced in transesterification reaction is not pure and it will be very costly and not worthy to refine the crude glycerol to high pharmaceutical grade. Therefore, it is not profitable when glycerol is produced as by-product.

The price for GC is the highest compared with other by-products. The price of GC is high because the cost of manufacturing is high. GC is conventionally obtained from the transesterification of glycerol with ethylene carbonate or dialkyl carbonate in the industry. However, the separation of glycerol carbonate from ethylene glycol which is the by-product from the transesterification reaction is difficult due to the high boiling point for both chemical substances [22]. There are other alternatives to produce GC such as reacting glycerol with DMC catalyzed with lipase [5], carbamoylation–carbonation reaction between urea and glycerol [53], however the production of glycerol carbonate yield is low and unreliable. Until recently, the glycerol-free biodiesel production by using supercritical DMC technology was proven to be able to produce GC as by-product in a promising quantitative yield [54]. Hence, the revenue of the GC is high enough to make this method economical and beneficial to the biodiesel manufacturers.

In Table 4, the price for the glyoxal 40% in aqueous solution is higher than glycerol. In the transesterification between FFA and DMC, glyoxal in water can be obtained. Although the glyoxal obtained was not pure with unknown percentage, it can be easily subjected to further purification step in order to meet the requirement for the commercial glyoxal in the commercial market. Thus, this could be a wise choice for biodiesel manufacturers to increase their revenue by producing glyoxal instead of the lowly priced glycerol.

The price for TAG is also higher than glycerol, implying that the production of TAG could also increase the revenue in biodiesel production. Moreover, TAG can be used as fuel in engine combustion. The conversion of 125% of fuel from one molecule of TG can be achieved by using the glycerol-free supercritical MA technology. The quality of the biodiesel in engine performance would be increased with the presence of TAG. The viscosity, density of the BDF is within the regulated guidelines; the decrease of the pour point and the higher heating value can make the BDF to perform a better combustion in the engine.

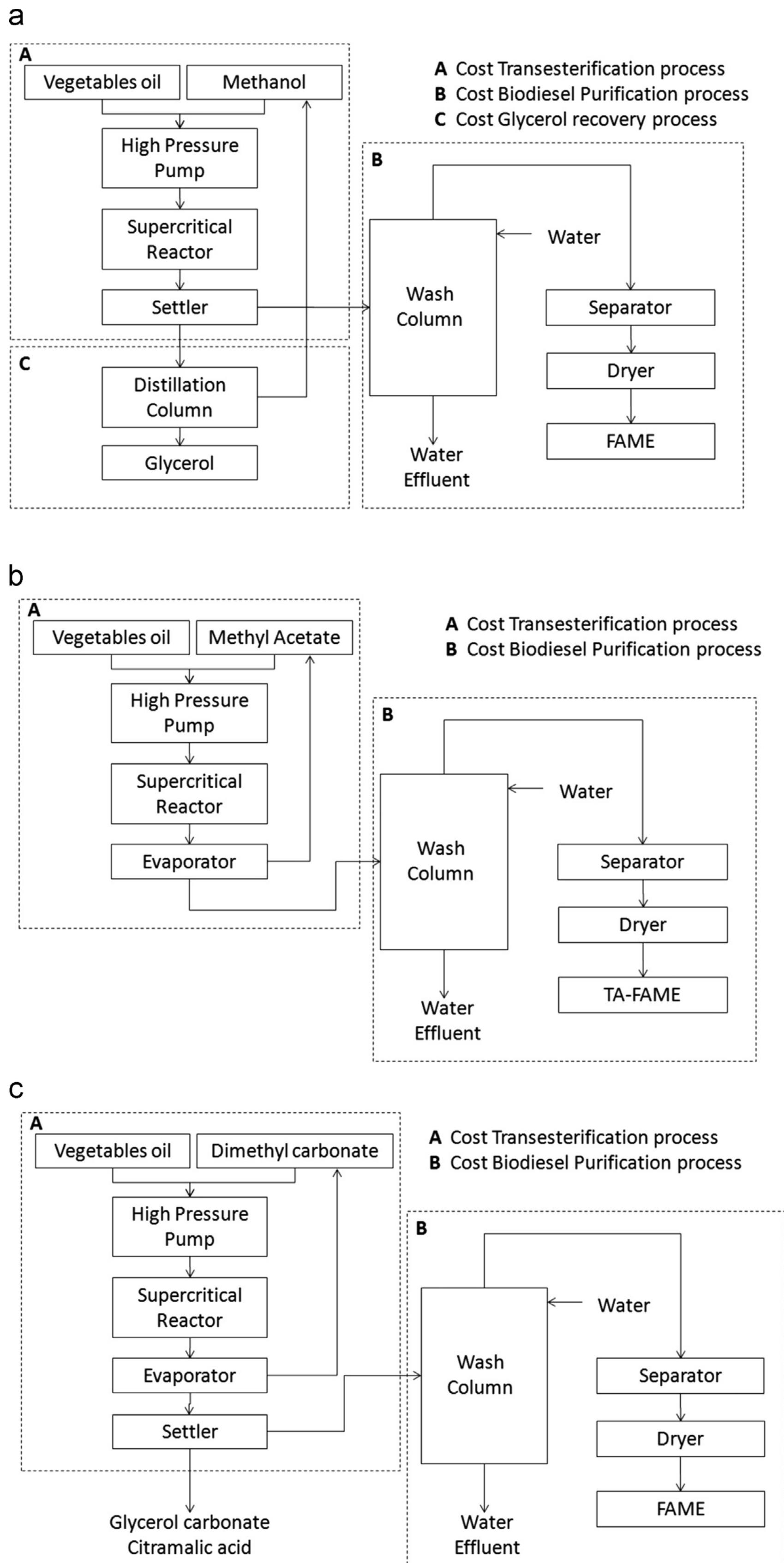


Fig. 1. Block flow diagram for (a) SCM, (b) SCMA, and (c) SCDMC process for biodiesel production.

Other than that, comparison was made between the prices of glycerol and some biodiesel additives as shown in Table 4 which have similar effects of TAG in biodiesel. There are many types of biodiesel additives that have different function to the biodiesel. For example, Polar Power, Total Power, 8+ Cetane Improver from the supplier of Biodiesel-Kit-Online [55]. These are the common

Table 4
Price for the by-product of the supercritical fluid transesterification and biodiesel additives.

Chemicals	Price[a] (USD/liter)	Supplier/brand
By-product		
Glycerol 99%	46.75	Acros
Glyoxal 40 wt% in water	60.60	Acros
Glycerol carbonate	1036.00	TCI America
Triacetin 99%	68.00	Acros
Biodiesel additives		
Polar power	13.15	
Total power	15.00	Biodiesel-Kit-Online
8+ Cetane improver	17.38	

[a] Prices of the chemical substances are based on the chemical suppliers (year 2013).

Table 5
Price for reactants and products in the transesterification reaction.

Chemicals	Price[a] (USD/mol)	Suppliers
Triglyceride/palm oil	0.93	Hin Lee Sawit oil
Methanol	0.20	Acros
Methyl acetate	2.14	Acros
Dimethyl carbonate	6.47	Acros
Glycerol	3.20	Acros
Triacetin	12.85	Acros
Glycerol carbonate	87.39	TCI America

[a] Prices of the chemical substances are based on the chemical suppliers (year 2013).

Table 6
Gross profit margin analysis between SCM with SCMA and SCDMC for biodiesel production.

	SCM	SCMA	SCDMC
Cost of materials (USD) (1 mol TG+3 mol reactant)	1.54	7.36	20.35
Sales of products (USD) (1 mol by-product)	3.40	12.85	87.39
Gross profit margin (%)	54.60	42.69	76.71

additives to be added in biodiesel in order to improve the engine performance. These additives could decrease the pour point of the biodiesel to make it applicable in cold climate countries. In Table 4, it is clearly shown that the prices for these biodiesel additives are slightly lower than TAG. Once again, it is proven that glycerol in biodiesel production is not beneficial to biodiesel manufacturers; instead glycerol-free production with biodiesel additives such as TAG or other valuable by-product should be carried out in the industry.

Lastly, economic analysis based on the gross profit margin was carried on the SCM with glycerol-free processes which are SCMA and SCDMC in Table 6. Gross profit margin is defined as the percent of total sales revenue retains after incurring the cost of goods sales (COGS) associated in the production [56] as shown in Eq. (7). Cost of goods sold (COGS) in this case referred to the raw materials as all the operating condition among SCM, SCMA and SCDMC was similar at supercritical conditions. Higher percentage of gross profit margin indicates that the process would be giving higher revenue to manufacturers. Other than that, the analysis was done without the sales of FAME, as it is assumed that same amount and quality of FAME is produced from one mole of TG in these three processes.

$$\text{Gross profit margin} = \frac{\text{Sales revenue} - \text{Cost of goods sold (COGS)}}{\text{Sales revenue}} \times 100\% \quad (7)$$

From Table 6, it is apparent that the SCDMC process is having the highest gross profit margin at about 76.71%, followed by SCM with 54.60%. With higher percent of profit margin, it indicates that SCDMC process would be gaining more profit compared with the conventional SCM method. Hence, the costs involved in supercritical fluid operation which required high temperature and pressure could be compensated and leads to competitive biodiesel processing. As a conclusion, glycerol-free processes had shown its potential to be implemented in the industry.

6. Conclusion

Biodiesel production by using glycerol-free process via supercritical technology has been gaining a lot of attention from researches. However, by using this method, there are many considerations that should be taken into account such as the energy consumption and the marketability of by-products. From economic perspective, the low price of the glycerol is not beneficial to the biodiesel manufacturers. Instead, glycerol-free process via supercritical technology with other valuable by-product should be carried out in the industry. By-products such as glycerol carbonate and triacetin are found to give higher revenue compared to glycerol which could lead to higher gross profit margin in biodiesel production.

Acknowledgment

The authors would like to acknowledge Universiti Sains Malaysia (Research University Grant No.1001/PJKIMIA/814047) and Ministry of Higher Education, Malaysia for the financial support given.

References

[1] Kumar A, Nerella VKV. Experimental analysis of exhaust emissions from Transit Buses fuelled with biodiesel. Open Environ Eng J 2009;2:81–96.
[2] Rosa CD, Morandim MB, Ninow JL, Oliveira D, Treichel H, Oliveira JV. Lipase-catalyzed production of fatty acid ethyl esters from soybean oil in compressed propane. J Supercrit Fluids 2008;47:49–53.
[3] Song E-S, Lim J-w, Lee H-S, Lee Y-W. Transesterification of RBD palm oil using supercritical methanol. J Supercrit Fluids 2008;44:356–63.
[4] Kansedo J, Lee KT, Bhatia S. Biodiesel production from palm oil via heterogeneous transesterification. Biomass Bioenergy 2009;33:271–6.
[5] Kim SC, Kim YH, Lee H, Yoon DY, Song BK. Lipase-catalyzed synthesis of glycerol carbonate from renewable glycerol and dimethyl carbonate through transesterification. J Mol Catal B: Enzym 2007;49:75–8.
[6] Saka S, Kusdiana D. Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. Fuel 2001;80:225–31.
[7] Hawash S, Kamal N, Zaher F, Kenawi O, Diwani GE. Biodiesel fuel from Jatropha oil via non-catalytic supercritical methanol transesterification. Fuel 2009;88:579–82.
[8] Kusdiana D, Saka S. Effects of water on biodiesel fuel production by supercritical methanol treatment. Bioresour Technol 2004;91:289–95.
[9] Tan KT, Lee KT, Mohamed AR. Effects of free fatty acids, water content and co-solvent on biodiesel production by supercritical methanol reaction. J Supercrit Fluids 2010;53:88–91.
[10] Demirbas A. Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification. Energy Convers Manag 2009;50:923–7.
[11] Thurmond W. Biodiesel 2020: a global market survey ⟨http://www.emerging-markets.com/biodiesel/default.asp⟩; 2008.
[12] Pachauri N, He B. Value-added utilization of crude glycerol from biodiesel production: a survey of current research activities. ASABE Pap 2006:1–16.
[13] Saka S, Isayama Y, Ilham Z, Jiayu X. New process for catalyst-free biodiesel production using subcritical acetic acid and supercritical methanol. Fuel 2010;89:1442–6.
[14] Pagliaro M, Rossi M. Glycerol: properties and production. The future of glycerol: new usages for a versatile raw material. 2nd ed. Royal Society of Chemistry; 2008. p. 1–28.
[15] Shin H-Y, Lim S-M, Kang SC, Bae S-Y. Statistical optimization for biodiesel production from rapeseed oil via transesterification in supercritical methanol. Fuel Process Technol 2012;98:1–5.
[16] Gui MM, Lee KT, Bhatia S. Supercritical ethanol technology for the production of biodiesel: process optimization studies. J Supercrit Fluids 2009;49:286–92.

[17] Tan KT, Gui MM, Lee KT, Mohamed AR. An optimized study of methanol and ethanol in supercritical alcohol technology for biodiesel production. J Supercrit Fluids 2010;53:82–7.
[18] Lee JS, Saka S. Biodiesel production by heterogeneous catalysts and supercritical technologies. Bioresour Technol 2010;101:7191–200.
[19] Sawangkeaw R, Teeravitud S, Bunyakiat K, Ngamprasertsith S. Biofuel production from palm oil with supercritical alcohols: effects of the alcohol to oil molar ratios on the biofuel chemical composition and properties. Bioresour Technol 2011;102:10704–10.
[20] García E, Laca M, Pérez E, Garrido A, Peinado Jn. New class of acetal derived from glycerin as a biodiesel fuel component. Energy Fuels 2008;22:4274–80.
[21] Saka S, Isayama Y. A new process for catalyst-free production of biodiesel using supercritical methyl acetate. Fuel 2009;88:1307–13.
[22] Ochoa-Gómez JR, Gómez-Jiménez-Aberasturi O, Maestro-Madurga B, Pesquera-Rodríguez A, Ramírez-López C, Lorenzo-Ibarreta L, et al. Synthesis of glycerol carbonate from glycerol and dimethyl carbonate by transesterification: catalyst screening and reaction optimization. Appl Catal A: General 2009;366:315–24.
[23] Fabbri D, Bevoni V, Notari M, Rivetti F. Properties of a potential biofuel obtained from soybean oil by transmethylation with dimethyl carbonate. Fuel 2007;86:690–7.
[24] Ilham Z, Saka S. Dimethyl carbonate as potential reactant in non-catalytic biodiesel production by supercritical method. Bioresour Technol 2009;100:1793–6.
[25] Iijima W, Kobayashi Y, Takekura K, Kato H, Taniwaki K. The non-glycerol process of biodiesel fuel treated in supercritical methanol. In: ASAE/CSAE annual international meeting, vol. 60; 2005. p. 512–6.
[26] Tundo P. New developments in dimethyl carbonate chemistry. Pure Appl Chem 2001;73:1117–24.
[27] Goembira F, Matsuura K, Saka S. Biodiesel production from rapeseed oil by various supercritical carboxylate esters. Fuel 2012;97:373–8.
[28] Ilham Z, Saka S. Optimization of supercritical dimethyl carbonate method for biodiesel production. Fuel 2012;97:670–7.
[29] Cross J, Hunter R, Stimson V. The thermal decomposition of simple carbonate esters. Aust J Chem 1976;29:1477–81.
[30] Imahara H, Minami E, Hari S, Saka S. Thermal stability of biodiesel in supercritical methanol. Fuel 2008;87:1–6.
[31] Tan KT, Lee KT, Mohamed AR. Optimization of supercritical dimethyl carbonate (SCDMC) technology for the production of biodiesel and value-added glycerol carbonate. Fuel 2010;89:3833–9.
[32] Goembira F, Saka S. Optimization of biodiesel production by supercritical methyl acetate. Bioresour Technol 2013;131:47–52.
[33] Goembira F, Saka S. Factors affecting biodiesel yield in interesterification of rapeseed oil by supercritical methyl acetate. In: Yao T, editor. Zero-Carbon Energy Kyoto 2011. Japan: Springer; 2012. p. 147–52.
[34] Campanelli P, Banchero M, Manna L. Synthesis of biodiesel from edible, non-edible and waste cooking oils via supercritical methyl acetate transesterification. Fuel 2010;89:3675–82.
[35] Tan KT, Lee KT, Mohamed AR. A glycerol-free process to produce biodiesel by supercritical methyl acetate technology: an optimization study via response surface methodology. Bioresour Technol 2010;101:965–9.
[36] Niza N, Tan K, Ahmad Z, Lee K. Comparison and optimisation of biodiesel production from *Jatropha curcas* oil using supercritical methyl acetate and methanol. Chem Pap 2011;65:721–9.
[37] Niza NM, Tan KT, Lee KT, Ahmad Z. Biodiesel production by non-catalytic supercritical methyl acetate: thermal stability study. Appl Energy 2012.
[38] Niza NM, Tan KT, Lee KT, Ahmad Z. Influence of impurities on biodiesel production from *Jatropha curcas* L. by supercritical methyl acetate process. J Supercrit Fluids 2013;79:73–5.
[39] Doná G, Cardozo-Filho L, Silva C, Castilhos F. Biodiesel production using supercritical methyl acetate in a tubular packed bed reactor. Fuel Process Technol 2013;106:605–10.
[40] Ilham Z, Saka S. Two-step supercritical dimethyl carbonate method for biodiesel production from *Jatropha curcas* oil. Bioresour Technol 2010;101:2735–40.
[41] Ilham Z, Saka S. Production of biodiesel with glycerol carbonate by non-catalytic supercritical dimethyl carbonate. Lipid Technol 2011;23:10–3.
[42] Kovvali AS, Sirkar KK. Carbon dioxide separation with novel solvents as liquid membranes. Ind Eng Chem Res 2002;41:2287–95.
[43] Yu RJ, Van Scott EJ. Method of treating wrinkles using citramalic acid. United States Patent 5,554,651; 1996.
[44] Shuit SH, Ong YT, Lee KT, Subhash B, Tan SH. Membrane technology as a promising alternative in biodiesel production: a review. Biotechnol Adv 2012;30:1364–80.
[45] Atadashi IM, Aroua MK, Aziz AA. Biodiesel separation and purification: a review. Renew Energy 2011;36:437–43.
[46] Lam MK, Lee KT, Mohamed AR. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review. Biotechnol Adv 2010;28:500–18.
[47] Tan KT, Lee KT. A review on supercritical fluids (SCF) technology in sustainable biodiesel production: potential and challenges. Renew Sustain Energy Rev 2011;15:2452–6.
[48] Kivevele TT, Mbarawa MM, Bereczky A, Laza T, Madarasz J. Impact of antioxidant additives on the oxidation stability of biodiesel produced from Croton Megalocarpus oil. Fuel Process Technol 2011;92:1244–8.
[49] Tesfa B, Mishra R, Gu F, Powles N. Prediction models for density and viscosity of biodiesel and their effects on fuel supply system in CI engines. Renew Energy 2010;35:2752–60.
[50] Casas A, JRn Ruiz, MaJs Ramos, Pérez An. Effects of triacetin on biodiesel quality. Energy Fuels 2010;24:4481–9.
[51] Jon Van G. Biodiesel processing and production. Fuel Process Technol 2005;86:1097–107.
[52] West AH, Posarac D, Ellis N. Assessment of four biodiesel production processes using HYSYS.Plant. Bioresour Technol 2008;99:6587–601.
[53] Climent MJ, Corma A, De Frutos P, Iborra S, Noy M, Velty A, et al. Chemicals from biomass: synthesis of glycerol carbonate by transesterification and carbonylation with urea with hydrotalcite catalysts. The role of acid-base pairs. J Catal 2010;269:140–9.
[54] Herseczki Z, Varga T, Marton G. Synthesis of glycerol carbonate from glycerol, a by-product of biodiesel production. Int J Chem React Eng 2009;7:87.
[55] Biodiesel-Kits-Online. Biodiesel additive 〈http://www.biodiesel-kits-online.com/biodiesel-additive.html〉; 2013.
[56] Bartram SM, Brown GW, Fehle FR. International evidence on financial derivatives usage. Financ Manag 2009;38:185–206.